

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

---

In re Patent Application of:  
Gerrit Luinstra et al.

Application No.: 10/523,263

Confirmation No.: 1826

Filed: March 7, 2005

Art Unit: 1626

For: CATALYST FOR THE CARBONYLATION OF  
OXIRANES

---

Examiner: R. T. Shiao

**REQUEST FOR RECONSIDERATION**

MS AF  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

**INTRODUCTORY COMMENTS**

In response to the Office Action dated November 26, 2007, the applicant respectfully requests reconsideration in view of the following remarks.

**Remarks/Arguments** begin on page 2 of this paper.

**REMARKS**

Applicant respectfully requests reconsideration in view of the following remarks. Claims 1-8 are rejected under 35 U.S.C. 102(a) as being anticipated by Allmendinger et al. publication, Z. Anorg. Allg. Chem., 2003, 629:1347-1352 ("Allmendinger"). Claims 1-8 are rejected under 35 U.S.C. 103(a) as being obvious over the Allmendinger. The applicant respectfully traverses these rejections.

The present application claims priority of German application DE 102 35 317.4, filed on August 1, 2002. Applicant submits herewith an English translation of priority document no. DE 102 35 317.4. The applicant believes that they are now entitled to benefit of their priority date. The publication that has been applied against the claims by the Examiner was published after the applicant's effective filing date. Therefore these rejections then should be withdrawn.

In view of the above response, applicant believes the pending application is in condition for allowance.

Applicant has paid for a one-month extension of time. Applicant believes no additional fee is due with this response. However, if a fee is due, please charge our Deposit Account No. 03-2775, under Order No. 13156-00001-US from which the undersigned is authorized to draw.

Dated: March 25, 2008

Respectfully submitted,

Electronic signature: /Ashley I. Pezzner/  
Ashley I. Pezzner  
Registration No.: 35,646  
CONNOLLY BOVE LODGE & HUTZ LLP  
1007 North Orange Street  
P. O. Box 2207  
Wilmington, Delaware 19899-2207  
(302) 658-9141  
(302) 658-5614 (Fax)  
Attorney for Applicant

Enclosure: English Translation of Priority Document DE 102 35 317.4

**TRANSLATION**

**THE FEDERAL REPUBLIC OF GERMANY**



**Priority Certificate  
on the Filing of a Patent Application  
DE 102 35 317.4**

**Application no.:** 102 35 317.4  
**Date of filing:** August 1, 2002  
**Applicant/Proprietor:** BASF Aktiengesellschaft, 67063 Ludwigshafen,  
Germany (DE)  
**Title:** Catalyst and process for the carbonylation of oxiranes  
**IPC:** C 07 303/02, B 01 J 31/02

The appended documents are a true and precise reproduction of the parts of the documentation of this patent application filed on August 1, 2002, irrespective of any color deviations stemming from the copying procedure.

Munich, January 23, 2008  
**German Patent and Trademark Office**  
**The President**  
By proxy

[Signed: illegible]

[Stamp:]  
Büchs

BASF Aktiengesellschaft

August 1, 2002  
B02/0101 IB/SF/ewe

5

---

**Catalyst and process for the carbonylation of oxiranes**

---

10

The invention relates to the preparation of lactones by means of the catalytic carbonylation of oxiranes in the presence of a catalyst system, to a corresponding catalyst system and to its use.

The catalytic carbonylation of simple and substituted oxiranes is a generally known procedure. It is often the case that the products are not the desired lactones, or the reaction conditions or the starting materials do not permit efficient preparation or isolation of lactones. The compounds can frequently be obtained only by means of complicated and costly syntheses.

JP-A-09 169 753 describes the carbonylation of epoxides to form lactones over  $\text{Co}_2\text{CO}_8$  as the catalyst in a straight-through reactor. The conversion rates are only 30%. This means that a separation and recirculation installation is required to achieve a high yield and purity of the lactone.

GB-A-1,020,575 relates to a process for the preparation of polymers of  $\beta$ -lactones. Carbon monoxide and a 1,2-epoxide are reacted to form a  $\beta$ -lactone as the intermediate product. This is carried out using octacarbonyldicobalt as the catalyst. In addition, it is possible to use a promoter selected from among metal halides such as potassium iodide and quaternary ammonium halides such as tetraethylammonium bromide. However, the yields of lactone

30

are less than 10% and the main fractions of the products are polyhydroxypropionic esters. Moreover, the reaction is carried out in a complicated manner using several pressure stages.

5 EP-B-0 577 206 relates to the carbonylation of epoxides over a catalyst system comprising a cobalt source and a hydroxy-substituted pyridine compound, especially 3-hydroxypyridine or 4-hydroxypyridine. The carbonylation is preferably carried out in the presence of a hydroxy compound such as water or alcohols. The activities of the catalysts used are relatively low, and the isolation of the lactones is not described. It has also been observed that a change in the reaction mixture occurs after the carbonylation has ended. Polymeriza-  
10 tion of the lactone takes place within 24 hours. This indicates that the lactone is not unreactive in the reaction mixture. It is also known that lactones can polymerize under the influence of pyridines.

Chemistry Letters 1980, pages 1549 to 1552, relates to the reaction of epoxides with carbon  
15 monoxide over a rhodium complex as the catalyst. The yields are 70% at the maximum.

J. Org. Chem. 2001, 66, pages 5424 to 5426, describes the synthesis of  $\beta$ -lactones by carbonylation of epoxides over cobalt and Lewis acid catalysts. A system comprising  $\text{PPNCo}(\text{CO})_4$  and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  is used as the catalyst. The yields are in the range from 7% to  
20 86%. However, the reaction time is from 7 to 24 hours, and it is necessary to use large amounts of catalyst.

J. Am. Chem. Soc. 124, No. 7, 2002, pages 1174 to 1175, describes the preparation of  $\beta$ -lactones by carbonylation of epoxides. The catalyst used is a mixture of a salt of aluminum  
25 salts and a tetracarbonylcobaltate. The handling and synthesis of the aluminum compound are complicated, so that the process cannot be carried out on a large industrial scale.

It is the objective of the invention to provide an uncomplicated and efficient process for the preparation of lactones by means of carbonylation of epoxides. Another objective is to provide a suitable catalyst system for this reaction.

5 This objective is achieved according to the invention by a process for the preparation of lactones by means of the catalytic carbonylation of oxiranes, characterized in that a catalyst system comprising

- a) at least one cobalt compound as component A and
- 10 b) at least one metal compound having the general formula (I) as component B,



15 wherein

- M is an alkaline earth metal or a metal of groups 3, 4 or preferably 12 or 13 of the periodic table of the elements,
- R is hydrogen or a hydrocarbon radical which can be substituted on the carbon
- 20 atoms, aside from the carbon atom bound to M,
- X is an anion,
- n is a number corresponding to the valence of M and
- x is a number in the range from 0 to n,

25 with n and x being selected in such a way that the result is a neutral charge,

is used as the catalyst.

The objective of the invention is also achieved by a catalyst as defined above except for the combination  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{Co}(\text{acac})_3$ .

5 The catalyst system  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{Co}(\text{acac})_3$  has already been described in Die Makromolekulare Chemie [Macromolecular Chemistry] 89, 1965, pages 263 to 268. This reference deals with the copolymerization of carbon monoxide with alkylene oxides and does not describe the formation of lactones.

10 Lactones are valuable compounds for the preparation of biodegradable polyesters; see, for example, EP-A-0 688 806. These polyesters are widely used, for example as polyols in polyurethane production or as a work material.

15 According to the invention, it has been found that a combination of cobalt compounds, in particular compounds in a low oxidation state, and metal compounds constitutes an efficient catalyst system for the gentle carbonylation of oxiranes to form lactones.

In the catalyst system used according to the invention, preference is given to 0.1 to 1000 mol, particularly preferably from 1 to 100 mol, of component B per mole of component A.

20 Component A is preferably selected in such a way that a cobalt carbonyl compound is present under the reaction conditions. This means that a cobalt carbonyl compound can be used directly as component A or it is possible to use a compound which is converted into a cobalt carbonyl compound under the reaction conditions.

25 R is preferably hydrogen or  $\text{C}_{1-32}$ -alkyl,  $\text{C}_{2-20}$ -alkenyl,  $\text{C}_{3-20}$ -cycloalkyl,  $\text{C}_{6-18}$ -aryl,  $\text{C}_{7-20}$ -aralkyl or  $\text{C}_{7-20}$ -alkaryl, whereby substituents can be present on the carbon atoms, aside from the carbon atom bound to M. R is preferably hydrogen or a monoanionic hydrocarbyl group, for example  $\text{C}_{1-32}$ -alkyl such as methyl, ethyl, i-propyl or n-propyl, i-butyl, n-butyl

or t-butyl, n-pentyl or n-hexyl, C<sub>2-20</sub>-alkenyl such as propenyl or butenyl, C<sub>3-20</sub>-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclopentadienyl or cyclohexyl, C<sub>6-18</sub>-aryl such as phenyl or naphthyl, and C<sub>7-20</sub>-arylalkyl, for example, benzyl (the preferred hydrocarbyl group is alkyl and particularly preferred hydrocarbyl groups are methyl or ethyl),

5

X is an anion such as halide (except for fluoride), sulfonate, oxide, C<sub>1-32</sub>-alkoxide, amide; preferred anions are halide or alkoxide, particularly preferably chloride or C<sub>1-12</sub>-alkoxide,

whereby n corresponds to the oxidation state OS or the valence of the metal and x is smaller than or equal to n and is not negative (for each oxide ligand,  $x = x + 1$ ).

10

Component B is preferably AlCl<sub>x</sub>R<sub>3-x</sub>, wherein x is a number from 0 to 3 and R is C<sub>1-6</sub>-alkyl. The numbers n and x can be integers or fractions. Fractions can arise in the case of a mixture of such compounds.

15

If desired, component A or B can also bind a neutral donor L in the coordination sphere. A donor L is generally a neutral compound containing oxygen, nitrogen or phosphorus atoms such as, for example, ethers, carbonates, ketones, sulfoxides, amines, amides, phosphanes, nitro functions or nitrile functions, etc. Donor L can also be an olefin or an aromatic compound.

20

Of course, it is also possible to use mixtures of several different components B and/or A as the catalyst system.

Particular preference is given to the combination of octacarbonyldicobalt and trimethylaluminum or octacarbonyldicobalt and triethylaluminum or octacarbonyldicobalt and tri(sec-butyl)aluminum, or octacarbonyldicobalt and tris(isopropoxy)aluminum.

25

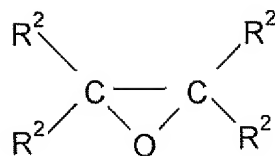
The carbonylation is generally carried out at elevated pressure and at an elevated temperature. However, product formation is also observed at a carbon monoxide pressure of one atmosphere. The pressure is generally generated by means of CO gas. In certain cases, the pressure can also be partially generated by means of an inert medium such as argon or nitrogen. The pressures in this case are in the range from 1 bar to 250 bar, preferably from 10 bar to 100 bar, particularly preferably from 20 bar to 60 bar. The reaction can generally be carried out at temperatures ranging from  $-10^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  [ $14^{\circ}\text{F}$  to  $392^{\circ}\text{F}$ ]. The preferred temperature ranges from  $20^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  [ $68^{\circ}\text{F}$  to  $302^{\circ}\text{F}$ ], particularly preferably from  $40^{\circ}\text{C}$  to  $110^{\circ}\text{C}$  [ $104^{\circ}\text{F}$  to  $230^{\circ}\text{F}$ ].

The carbonylation of epoxides can be conducted either batchwise or in a continuous process. It can be carried out either in the gas phase or in an inert reaction medium. This medium is generally a liquid. Such liquids are customary solvents such as ether, diglyme, triglyme, tetraglyme, tetrahydrofuran, dimethoxyethane, hydrocarbons such as hexane, octane, isopar, benzene, toluene, xylene, decalin; chlorinated hydrocarbons such as dichloromethane, dichloroethane, dichlorobenzene or polar solvents such as DMF, DMSO, esters, nitriles, nitro compounds, ketones or so-called ionic liquids. Preferred solvents are DME, diglyme, dichloromethane. Oxirane can also be used as reaction medium.

In order to further activate the catalyst system, it is possible to add donor ligands such as phosphanes or nitriles. The application of the catalyst components (for example, cobalt and alkyl compound) onto a particulate support material, for example, silica or aluminum oxide, makes it possible to carry out a solvent-free reaction along the lines of a gas-phase carbonylation.

Suitable oxirane compounds are ethylene oxide and substituted epoxides. These are usually compounds having the general formula (II):

- 7 -



(II)

In this formula, the radicals  $\text{R}^2$ , independently of one another, each stand for hydrogen, halogen, a nitro group  $-\text{NO}_2$ , a cyano group  $-\text{CN}$ , an ester group  $-\text{COOR}^3$  or a hydrocarbon group having from 1 to 32 carbon atoms, which can be substituted. Some or all of the radicals  $\text{R}^2$  in a compound (II) can be the same or else they can be four different radicals.  $\text{R}^3$  can be  $\text{C}_{1-12}$ -alkyl or aryl.

It is preferable to make use of geminally substituted epoxides, particularly preferably epoxides substituted only in the 1-position.

Examples of suitable hydrocarbon groups are  $\text{C}_{1-32}$ -alkyl such as methyl, ethyl, i-propyl or n-propyl, i-butyl, n-butyl or t-butyl, n-pentyl or n-hexyl,  $\text{C}_{2-20}$ -alkenyl such as propenyl or butenyl,  $\text{C}_{3-20}$ -cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, aryl such as phenyl or naphthyl, and  $\text{C}_{7-20}$ -arylalkyl, for example, benzyl. Here, if two radicals  $\text{R}^2$  are located on different carbon atoms of the epoxy group, they can be bridged to each other so as to form a  $\text{C}_{3-20}$ -cycloalkylene group.

Substituents with which the  $\text{C}_{1-32}$ -hydrocarbon group or R above can be substituted, comprise in particular, the following groups: halogen, cyano, nitro, thioalkyl, *tert*-amino, alkoxy, aryloxy, arylalkyloxy, carbonyldioxyalkyl, carbonyldioxyaryl, carbonyldioxyarylalkyl, alkoxycarbonyl, aryloxy carbonyl, arylalkyloxycarbonyl, alkylcarbonyl, arylcarbonyl, arylalkylcarbonyl, alkylsulfinyl, arylsulfinyl, arylalkylsulfinyl, alkylsulfonyl, arylsulfonyl and arylalkylsulfonyl.

The oxirane compound used is preferably ethylene oxide, propylene oxide, butylene oxide (1-butene oxide, BuO), cyclopentene oxide, cyclohexene oxide (CHO), cycloheptene oxide, 2,3-epoxypropyl phenyl ether, epichlorohydrin, epibromohydrin, i-butene oxide (IBO), styrene oxide or acryl oxide. Particular preference is given to using ethylene oxide (EO),  
5 propylene oxide (PO), butylene oxide or i-butene oxide, very particularly preferably ethylene oxide or propylene oxide or mixtures thereof.

The oxirane compounds to be used for the process according to the invention can be obtained, for example, by epoxidation of terminal olefins using methods known to those  
10 skilled in the art. If the epoxidation occurs stereounspecifically, racemate cleavage has to be carried out. Methods for racemate cleavage, for example, by means of HPLC chromatography using a chiral column material, are known to those skilled in the art. The oxirane compound is advantageously prepared directly in enantiomerically pure or optically enriched form from a terminal olefin by means of established stereoselective processes. A  
15 suitable process is, for example, the so-called Sharpless epoxidation (see J. Am. Chem. Soc. 1987 (109), p. 5765 ff. and 8120 ff.; and "Asymmetric Synthesis", edited by J.D. Morrison, Academic Press, New York, 1985, Volume 5, Chapters 7 and 8).

Furthermore, optically enriched oxirane compounds are obtained from terminal olefins or  
20 racemic terminal epoxides by the methods described by Jacobsen *et al.*, Tetrahedron Lett. 1997, 38, pages 773 to 776; and in J. Org. Chem. 1998, 63, pages 6776 to 6777, which are also simple to carry out on a large industrial scale (see also Acc. Chem. Res. 2000, 33, pages 421 to 431).

25 It is also possible to prepare optically enriched oxirane compounds by mixing an appropriate amount of the racemate with the enantiomerically pure oxirane compound.

As compounds having a terminal double bond, it is fundamentally possible to use all olefins of this class of compounds, for example, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene or 1-octene.

5 Generally speaking, the reaction is conducted in such a way that the cobalt complexes (A) and the, for example, alkyl compounds (B) are first introduced into the reaction vessel either individually, simultaneously or in premixed form, if appropriate with cooling. It is also possible, if desired, for the oxirane compound to be mixed into the solution/suspension of the catalyst components before the latter is transferred to the reaction vessel. Further-  
10 more, the oxirane compound can also be introduced directly into the reaction vessel. The carbonylation is preferably carried out under inert conditions, that is to say, in the absence of moisture and air.

The termination of the reaction and the separation and purification of the lactones can be  
15 carried out by generally known methods. For example, the lactone can be isolated in a simple manner by distillation or crystallization.

The process according to the invention makes it possible to obtain 3-hydroxypropionic acid lactones from the corresponding enantiomerically pure oxirane compounds. If these oxirane  
20 compounds are used in optically enriched form, lactones are obtained whose the degree of optical purity corresponds directly to the degree in the oxirane. Lactones prepared in this manner can be used to establish the thermoplastic property profile of this class of biodegradable polymers, whose properties can be set very simply and specifically for the envisaged applications.

25

The advantages according to the invention can be seen in the simple operation and in the high activity and productivity of the carbonylation catalysis and of the commercially available catalyst components.

The invention also relates to a process for the preparation of the catalyst used according to the invention by mixing the components A und B. The invention also relates to the use of the catalyst in carbonylation reactions.

## 5    **Chemicals**

The chemicals used were made by Fluka, Aldrich or Merck and were used without any further purification. The solvents were dried over molecular sieves and, in each case, degassed before use. The aluminum alkyl compounds were used as solutions in toluene.

## 10   **Analysis**

NMR spectra were recorded on a Bruker AMX400 spectrometer. The IR measurements (KBr or directly as solution) were carried out on Bruker IFS 113V and IFS 66V instruments. For on-line IR studies to determine the reaction kinetics, a ReactIR<sup>TM</sup> (SiComp<sup>TM</sup> Dippersystem) made by Mettler Toledo was employed in a 250-ml Büchi reactor.

15

## **General procedure:**

The desired amount of epoxide (see Tables 1 to 4) was added to octacarbonyldicobalt  $\text{Co}_2\text{CO}_8$  (1 eq.) in diglyme at 0°C [32°F] under an argon atmosphere. A compound of type B (1-6 eq.) was finally added (see Tables 1 to 4).

20

In order to fill the steel autoclave (100 ml or 250 ml), it was first evacuated and then charged under a countercurrent of argon. After the starting materials had been transferred to the steel autoclave, a carbon monoxide pressure of 10 bar to 65 bar was set and the carbonylation was maintained at temperatures ranging from 75°C to 105°C [167°F to 221°F] for a prescribed period of time. The carbonylation was terminated by reducing the pressure to the ambient pressure, and the reaction solution obtained was cooled to 0°C [32°F], taken from  
25    the autoclave and analyzed. In order to separate off the catalyst, the resulting solution can be introduced into a mixture of diethyl ether and pentane. The catalyst and minute fractions

of polymer are separated off by filtration through silica gel, and subsequent fractional distillation of the filtrate yields the lactone in pure form.

The invention will be explained in greater depth with reference to the examples below.

5

## Examples

### Example 1:

Octacarbonyldicobalt  $\text{Co}_2\text{CO}_8$  (260 mg) is dissolved in 16 ml of diglyme, the solution is cooled to  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ] and 8 ml of propylene oxide are added. After the addition of 0.77 ml of a 2N solution of  $\text{Me}_3\text{Al}$  in toluene, the reaction mixture is transferred with the exclusion of moisture and oxygen to a 100-ml steel autoclave equipped with a glass liner. The carbonylation reaction is carried out at  $75^\circ\text{C}$  [ $167^\circ\text{F}$ ] under 60 bar of CO for 5 hours. The carbonylation reaction is terminated by reducing the pressure to the ambient pressure and cooling to  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ]. The analysis ( $^1\text{H}$ - and  $^{13}\text{C}$ -NMR) of a withdrawn sample reveals a complete carbonylation of the epoxide and a lactone yield  $> 95\%$  (the by-products are polyhydroxybutyrate and acetone).

### Example 2:

In a 250-ml steel autoclave equipped with an IR probe, octacarbonyldicobalt  $\text{Co}_2\text{CO}_8$  (780 mg) is dissolved in 50 ml of diglyme at  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ] under argon, and 26 ml of propylene oxide are added. After the addition of 7 ml of a 2N solution of  $\text{Me}_3\text{Al}$  in toluene, the autoclave is pressurized with 60 bar of CO. The carbonylation reaction is carried out at  $95^\circ\text{C}$  [ $203^\circ\text{F}$ ] under 60 bar of CO for 2 hours. The carbonylation reaction is terminated by reducing the pressure to the ambient pressure and cooling to  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ]. The analysis ( $^1\text{H}$ - and  $^{13}\text{C}$ -NMR) of a withdrawn sample reveals a complete carbonylation of the epoxide and a lactone yield  $> 95\%$  (the by-products are polyhydroxybutyrate and acetone).

### Example 3:

In a 250-ml steel autoclave equipped with an IR probe, octacarbonyldicobalt  $\text{Co}_2\text{CO}_8$  (780 mg) is dissolved in 50 ml of diglyme at  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ] under argon, and 26 ml of propylene oxide are added. After the addition of 7 ml of a 2N solution of  $\text{Me}_3\text{Al}$  in toluene, the autoclave is pressurized with 10 bar of CO. The carbonylation reaction is carried out at  $75^\circ\text{C}$  [ $167^\circ\text{F}$ ] under 10 bar of CO for 4 hours. To terminate the reaction, the pressure is brought down to the ambient pressure and the mixture is cooled to  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ]. The analysis ( $^1\text{H}$ - and  $^{13}\text{C}$ -NMR) of a withdrawn sample reveals a complete carbonylation of the epoxide and a lactone yield  $> 95\%$  (the by-products are polyhydroxybutyrate and acetone).

#### Example 4:

Octacarbonyldicobalt  $\text{Co}_2\text{CO}_8$  (130 mg) is dissolved in 8 ml of diglyme, the solution is cooled to  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ] and 7 ml of butyloxirane are added. After the addition of 0.39 ml of a 2N solution of  $\text{Me}_3\text{Al}$  in toluene, the reaction solution is transferred with the exclusion of moisture and oxygen to a 100-ml steel autoclave equipped with a glass liner. The carbonylation reaction is carried out at  $75^\circ\text{C}$  [ $167^\circ\text{F}$ ] under 60 bar of CO for 14 hours. The carbonylation reaction is terminated by reducing the pressure to the ambient pressure and cooling to  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ]. The analysis ( $^1\text{H}$ - and  $^{13}\text{C}$ -NMR) of a withdrawn sample reveals about 70% carbonylation of the epoxide and a lactone proportion of lactone in the product  $> 75\%$ .

#### Example 5:

Octacarbonyldicobalt  $\text{Co}_2\text{CO}_8$  (130 mg) and tetraethylammonium carbonylcobaltate  $\text{Et}_4\text{NCo}(\text{CO})_4$  (232 mg) are dissolved in 10 ml of diglyme, the solution is cooled to  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ] and 6 ml of propylene oxide are added. After the addition of aluminum isopropoxide ( $i\text{-PrO}$ ) $_3\text{Al}$ , the reaction solution is transferred with the exclusion of moisture and oxygen to a 100-ml steel autoclave equipped with a glass liner. The carbonylation reaction is carried out at  $75^\circ\text{C}$  [ $167^\circ\text{F}$ ] under 60 bar of CO for 16 hours. The carbonylation reaction is terminated by reducing the pressure to the ambient pressure and cooling to  $0^\circ\text{C}$  [ $32^\circ\text{F}$ ]. The analysis ( $^1\text{H}$ - and  $^{13}\text{C}$ -NMR) of a withdrawn sample reveals virtually complete carbonyla-

tion of the epoxide and a lactone yield > 85% (the by-products are polyhydroxybutyrate and acetone).

5 The following table is a compilation of further experiments which show that high conversion rates can be achieved in a short time using various combinations of cobalt compounds and component B.

**Table 1: Variation of the Al component**

No.	Catalyst	Epoxide	Reaction conditions	Yield
1	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (2 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/ 5h	Conversion 100% Lactone 96%
2	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Et <sub>3</sub> Al (2 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100% Lactone 91%
3	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) (i-Butyl) <sub>3</sub> -Al (2 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100% Lactone 87%
4	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/4h	Conversion 100% Lactone 92%
5	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (6 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/3h	Conversion 100% Lactone 88%
6	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) EtCl <sub>2</sub> Al (2 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100% Lactone 85%
7	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Et <sub>2</sub> ClAl ClEt <sub>2</sub> Al (1 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100% Lactone 90%
8	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) MAO (2 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/20h	Conversion 90% Lactone 80%
9	Co <sub>2</sub> CO <sub>8</sub> (0.5 eq.) Et <sub>4</sub> NCo(CO) <sub>4</sub> (1 eq.) (i-PrO) <sub>3</sub> Al (1 eq.)	PO (120 eq.)	75°C/60 bar of CO/ diglyme/16h	Conversion 100% Lactone 87%

All of the examples in Table 1 were carried out in a 100-ml steel autoclave equipped with a glass liner; the conversion rates and lactone proportion of lactone were determined by NMR measurements on a withdrawn sample; the by-products are polyhydroxybutyrate and, in small amounts, acetone.

**Table 2: Variation of the pressure**

No.	Catalyst	Epoxide	Reaction conditions	Yield
10	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (160 eq.)	75°C/80 bar of CO/ diglyme/5h	Conversion 100% Lactone 90%
11	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>2</sub> Al (4 eq.)	PO (160 eq.)	75°C/60 bar of CO/ diglyme/5h	Conversion 100% Lactone 93%
12	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (160 eq.)	75°C/40 bar of CO/ diglyme/5h	Conversion 100% Lactone 92%
13	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (160 eq.)	75°C/20 bar of CO/ diglyme/5h	Conversion 100% Lactone 91%
14	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (160 eq.)	75°C/10 bar of CO/ diglyme/5h	Conversion 100% Lactone 92%

All of the examples in Table 2 were carried out in a 250-ml steel autoclave without a glass liner and with IR reaction control; the conversion rates and proportions of lactone were determined by NMR measurements on a withdrawn sample; the by-products are polyhydroxybutyrate and, in small amounts, acetone.

**Table 3: Variation of the temperature**

No.	Catalyst	Epoxide	Reaction conditions	Yield
15	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (160 eq.)	95°C/60 bar of CO/ diglyme/2h	Conversion 100% Lactone 92%

16	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (160 eq.)	105°C/60 bar of CO/ diglyme/1h	Conversion 100% Lactone 91%
----	---	--------------	-----------------------------------	--------------------------------

All of the examples in Table 3 were carried out in a 250-ml steel autoclave without a glass liner and with IR reaction control; the conversion rates and proportions of lactone were determined by NMR measurements on a withdrawn sample; the by-products are poly-  
5 hydroxybutyrate and, in small amounts, acetone.

**Table 4: Variation of the epoxide-to-catalyst ratio**

No.	Catalyst	Epoxide	Reaction conditions	Yield
17	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (2 eq.)	PO (300 eq.)	75°C/60 bar of CO/ diglyme/10h	Conversion 100% Lactone 92%
18	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (600 eq.)	75°C/60 bar of CO/ diglyme/7h	Conversion 100% Lactone 94%
19	Co <sub>2</sub> CO <sub>8</sub> (1 eq.) Me <sub>3</sub> Al (4 eq.)	PO (1200 eq.)	75°C/60 bar of CO/ diglyme/16h	Conversion 80% Lactone 90%

10 All of the examples in Table 4 were carried out in a 100-ml steel autoclave equipped with a glass liner; the conversion rates and proportions of lactone were determined by NMR measurements on a withdrawn sample; the by-products are polyhydroxybutyrate and, in small amounts, acetone.

**Claims:**

5 1. A process for the preparation of lactones by means of the catalytic carbonylation of oxiranes, characterized in that a catalyst system comprising

- a) at least one cobalt compound as component A and  
10 b) at least one metal compound having the general formula (I) as component B,



15 wherein

- M is an alkaline earth metal or a metal of groups 3, 4 or preferably 12 or 13 of the periodic table of the elements,  
R is hydrogen or a hydrocarbon radical which can be substituted on the  
20 carbon atoms, aside from than the carbon atom bound to M,  
X is an anion,  
n is a number corresponding to the valence of M and  
x is a number in the range from 0 to n,

25 with n and x being selected in such a way that the result is a neutral charge,

is used as the catalyst.

2. The process according to claim 1, characterized in that component A is selected in such a way that a cobalt carbonyl compound is present under the reaction conditions.

5 3. The process according to claim 1 or 2, characterized in that M in the general formula (I) is Al, Mg, Zn or Sn.

4. The process according to any of claims 1 to 3, characterized in that, in the general formula (I), R is hydrogen or C<sub>1-32</sub>-alkyl, C<sub>2-20</sub>-alkenyl, C<sub>3-20</sub>-cycloalkyl, C<sub>6-18</sub>-aryl,  
10 C<sub>7-20</sub>-aralkyl or C<sub>7-20</sub>-alkaryl, whereby substituents can be present on the carbon atoms, aside from than the carbon atom bound to M,

and/or X is Cl, Br, I, sulfonate, oxide, C<sub>1-32</sub>-alkoxide or amide.

15 5. The process according to any of claims 1 to 4, characterized in that component B is AlCl<sub>x</sub>R<sub>3-x</sub>, wherein x is a number from 0 to 3 and R is C<sub>1-6</sub>-alkyl.

6. A catalyst as defined in any of claims 1 to 5, except for the combination Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>/Co(acac)<sub>3</sub>.

20

7. The process for the preparation of catalysts according to claim 6, by mixing components A and B.

8. The use of a catalyst according to claim 6 in carbonylation reactions.

25

**Abstract**

5

Lactones are prepared by means of the catalytic carbonylation of oxiranes using a catalyst system comprising

- a) at least one cobalt compound as component A and
- 10 b) at least one metal compound having the general formula (I) as component B,



(I)

15

wherein

M is an alkaline earth metal or a metal of group 3, 4 or preferably 12 or 13 of the Periodic Table of the Elements,

20

R is hydrogen or a hydrocarbon radical which can be substituted on the carbon atoms, aside from than the carbon atom bound to M,

X is an anion,

n is a number corresponding to the valence of M and

x is a number in the range from 0 to n,

25

with n and x being selected in such a way that the compound is uncharged,

as the catalyst.